

THE

AMERICAN JOURNAL OF SCIENCE

[FOURTH SERIES.]

18 Jan 15
ART. VII.—*On an Artificial Lava-Flow and its Spherulitic Crystallization*; by L. V. PIRSSON. (With Plate I.)

THE material which forms the basis of the following article, was obtained a number of years ago by the late Prof. Chas. E. Beecher, of Yale University, at Kane, an industrial town with glass-works, in McKean county, Penn., and presented to the writer. It appears that one of the furnaces in the glass-works accidentally broke, allowing the molten glass to escape; it flowed into the pit below and cooled there. When cold the mass of glass was blasted out and the broken material piled on one side. It was from this broken material that the specimens were obtained. The furnace is stated to have been 60 feet long by 25 feet wide, and the molten glass in it at the time to have been from 4 to 5 feet deep. This would have made about 6000 cubic feet of glass, or say 700,000 pounds, an amount which formed a flow of no mean size, when viewed from the experimental standpoint. During the flow and while cooling it partially crystallized, assuming features which it is the object of this paper to present. An accident of this kind to a glass furnace by which a flow of molten glass was produced, which partly crystallized, has been described by the late Professor Fouqué.* In this case portions of the glass were filled with milky white nodules with a greenish cast of color, which were in places the size of a nut. These nodules were spherulites which Fouqué proved to consist of radially fibrous prisms of wollastonite. Thanks to the kindness of Professor A. Lacroix of the Musée d'histoire naturelle in Paris the writer has been able to examine some of the glass described by Fouqué and to confirm his conclusions. The present material, while resembling it in some respects, differs in several important particulars, as will be presently shown.

* Compt. Rendus, cix, Jan. 1, 1889.

Morozewicz* has also described crystallizations resulting from the outflowing of glass from industrial furnaces; in this case large single crystals of wollastonite were formed. He mentions also rounded aggregates of fibrous diopside, but does not describe them definitely as of spherulitic structure.

Spherulites.—The most important kind of crystallization shown by the Kane glass-flow is in the formation of spherulites. The glass itself is an ordinary green bottle glass, pale greenish where thin and a clear, sea-green when a couple of inches thick or more. This is more or less filled with white spherical bodies which vary in size from that of very fine shot up to those which are nearly the size of an egg. These, and especially the largest ones, may be readily broken out of the glass, either as single spheroids, or as grouped or botryoidal masses. When extracted they have a smooth, thin, outer shell of glass which covers them like a skin. These solid bodies when broken open are white, with a pale greenish tinge, and are seen to possess a fibrous radiated structure. The fibers are extremely fine and thread-like, giving to the surface the luster of floss silk. This is true even in the largest. In some the cross section of the broken spherule, as it lies in the glass, appears radial but uniform, while in others changes in the conditions of crystallization, as the fibers grew outwardly from the center, have produced a series of concentric rings, such as are sometimes observed in the smaller spherulites in rhyolite. As many as ten of these rings, of almost perfectly circular form and of similar width, have been observed in one spherulite, and, thus mottling the silky sheen of the surface of the section of the divided spherulite, they have a moiré, or concentric, watered-silk appearance, and add greatly to its beauty. The structure, or consistency, of the spherulites varies greatly; some are so compact that they are composed almost wholly of crystalline material, while in others the thread-like fibers are relatively widely separated and the whole spherulite is saturated with the greenish glass. Thus, while the first form very solid white objects, the latter appear almost like misty or cloudy forms in the green matrix surrounding them, and the conchoidal fracture passes through the glass without reference to them nor can they of course be broken out and separated from it.

In another portion of the flow which formed a sheet about two inches thick the spherulites have a somewhat different character. Here they appear to be composed, not of tenuous fibers, but of distinct, rather thick, blades, 0.5–1.0^{mm} broad by 4^{mm} long, as may be seen by reference to figs. B and C in Plate I which represents them in very nearly natural size.

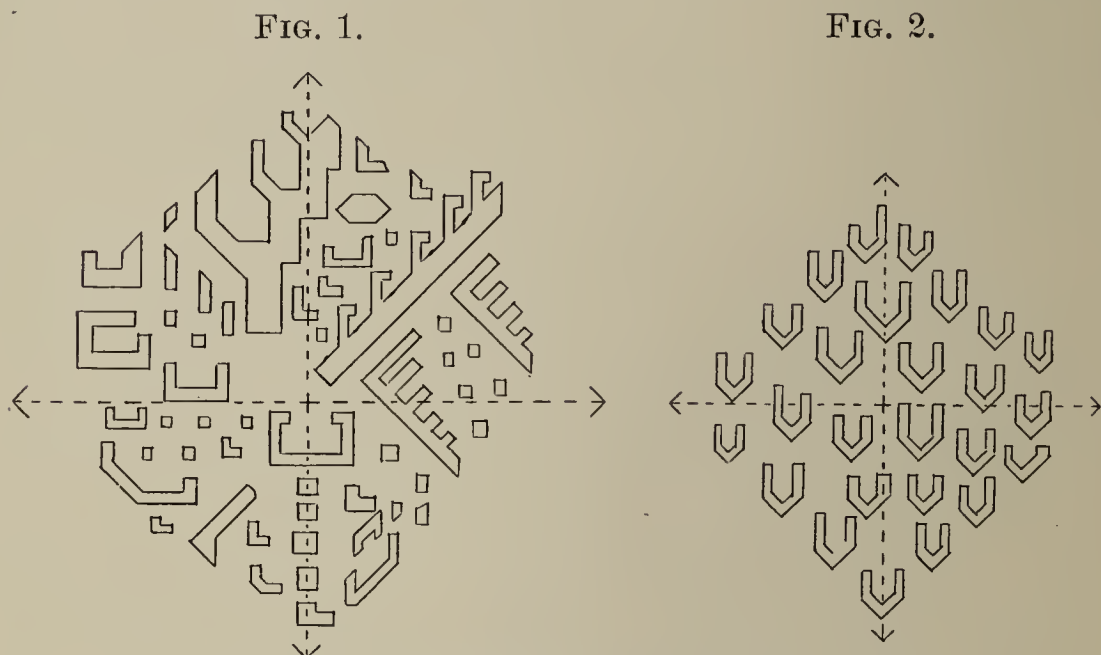
* Min. Petr. Mitt., xviii, p. 124, 1898.

They average about 7-8^{mm} in diameter. In addition to the regular spherulites various modifications of them exist in this place, as may be seen by reference to the plate. Some are composed of only a few blades, or even only two or three, radiating from a center in a star-like group, but with blades the same size and length as those of the more complete spherulites. The beauty of these white radiate and stellate crystallizations suspended in the clear sea-green glass is very striking, and the fact that they are thus suspended and did not fall to the bottom shows that at the time of their formation the molten glass was in too viscous a condition to permit of such movement, a fact whose bearing upon the question of their origin will be treated later. The bottom of this sheet of glass is composed of a layer of spherulites about 3-4^{mm} in thickness. Looking at the bottom surface itself it appears flat and smooth but so thickly covered with the radiate crystallizations of these spherulites, seen in half section, that they nearly everywhere coalesce, or are contiguous. The appearance recalls surfaces covered with radiate zeolites or frosted window-panes in winter. The upper surface of this layer presents a somewhat mossy appearance as the rounded, bladed, surfaces of the spherulites project into the glass. It is seen on the right hand side of figs. B and C in the plate. The white cloudy area near the top of the piece in fig. C is due to the internal reflection of light in the glass and nearly conceals a very fine spherulite. The blades composing these spherulites are small at the center where they unite and grow larger gradually as they extend into the glass. They are four sided with apparent right angles and are terminated by an oblique plane, but the crystallization is rough and imperfect. Close inspection of the photograph will show these details.

Mineral Composition.—The study of the mineral composing these spherulites in thin sections and in powdered grains under the microscope proves that it is artificial diopside. This is seen from the following properties: inclined extinction, c on c measured to a maximum of 39° ; sections having parallel extinction show the exit of an optic axis on the edge of the field and that the plane of the optic axes lies in the clinopinacoid parallel to the length of the prism; by repeatedly measuring the width of the nearly square prisms as they lie in the glass their thickness is also obtained, and the birefringent color yielded by those having the maximum angle of extinction indicates that the maximum birefringence is about 0.03. The cross section of the prisms shows them to be nearly square, but they are too minute to show the cleavage parallel to the prismatic sides; the extinction bisects the angle. These are the properties of diopside and the physical determination was confirmed

by qualitative chemical tests on material extracted from the glass which proved, in addition to the silica, the presence of traces of iron and alumina and abundant lime and magnesia. It is evident that a dolomite limestone was used in the making of the glass.

Microstructure of Crystals.—When studied under the microscope in powdered form it is found that the crystal blades, illustrated in the photographic plate, are very far from being the solid continuous crystals they appear. Close inspection of them with a simple lens, as they lie in the glass, proves them to have a parallel fibrous structure. The microscope



FIGS. 1, 2. Skeleton crystals of diopside.

shows them in length sections to consist of bundles of extremely slender rods or fibers. These are sometimes closely packed, sometimes separated by much more than their own diameters. They are surrounded by, or are cemented together, by the glass in which they lie. Sections across these fibrous bundles, or blades, prove that to a great degree they are not simple solid fibers, or rods, but are more or less hollow, or skeleton-like in form, and that groups of them have a similar crystallographic orientation. One of these is shown in the adjoining fig. 1. The directions of extinction in this are indicated by the broken arrow lines; these indicate the plane of symmetry in the compound or skeleton crystal and it is interesting that the directions of growth are along both pinacoidal and prismatic faces. Another type is shown in fig. 2; the growth here is along the clinopinacoid $b, 010$, and the prismatic faces; that along the orthopinacoid being wanting. A number of different patterns of growth were observed but they are sufficiently illustrated by these examples.

Chain Spherulites.—An interesting feature is the presence of chain spherulites along flowage lines, as illustrated in the photographic plate fig. A. The white lines are composed of layers of innumerable minute spherulites, while the darker layers between are of clear green glass free from crystalline products. Examination with a lens reveals the fact that almost without exception these lines are composed of a chain, or layer, of single spherulites. Generally they are so closely crowded that they coalesce to a considerable extent, less often they touch at the circumference, and in some places they appear quite regularly spaced but separated by areas of glass, generally not wider than their own diameter. Viewed with the lens from above, a layer appears like one of minute white pills sifted into the glass, innumerable in number and spread without order, here thickly clustered, there more thinly distributed. The average size of these spherulites is $0.5-0.6^{\text{mm}}$ and they do not vary much from it. Under the microscope in thin section they appear like the spherulites of feldspar seen in acid lavas, so much so that it is almost difficult to believe one is not dealing with a section of rhyolite. Although snow-white in the glass, and also as seen by the microscope with reflected light from the section, they appear of a light leather-brown color by transmitted light. With a low magnification the central part of the spherulite looks uniform and homogeneous, the fibrous character appears more evident as the outer boundary is approached, and the outermost zone is composed of distinct, branching, fibrous rays. With high magnification the central part is also resolved into masses of excessively fine, tenuous, matted fibers. At the center, where these fibers are cut perpendicularly, they appear as mere points.

When the structure of these bodies is revealed by the use of crossed nicols, it is seen that they are not formed uniformly of single fibers radiating from a common center, but rather of groups, or bundles, of fibers somewhat radially divergent, like brooms, or brushes; closely stellate groupings of which form the spherulites. Thus they repeat on a minute scale the examples shown in B and C of the plate and described in the preceding section. Like other spherulites they show a black cross, which is sometimes in one bundle, or brush, parallel with the planes of the nicols and sometimes, as the spherulite is revolved and a new brush comes into position, is somewhat inclined, proving that in each brush the majority of the minute fibers tend to have orientated positions and thus make a compound skeleton crystal. This is also like the larger ones described and figured in the preceding section.

The light leather-brown color of the sections of these spherulites is a curious feature. It is strongest in the central areas

where the fibers are finest and most closely packed; at the periphery, where they are coarser and more individualized, it is wanting. With a very high magnification of the center and parallel light from below, it disappears. With low-powered objectives it is present, whether the lower nicol is present or not. The spherulites of feldspars in acid volcanic lavas often show the same phenomenon of brown coloration, and so do the closely packed aggregates of minute scales of kaolin in feldspar. Since in all these cases the component mineral fibers, or scales, are white, that is to say colorless, this effect cannot be due to a pigment, but must be an optical phenomenon due to the absorption of light. An explanation of this may be somewhat as follows: Angular fibers or scales of a colorless mineral lying in all positions in a medium of lower refractive index may act as prisms to rays of light passing through them. The rays of white light would be then decomposed into their primary colors, and the violet rays more inclined than those of the red. On passing upward and striking inclined surfaces of new fibers, or scales, the light in the violet end of the spectrum, on account of its greater inclination than that towards the red end, would tend in greater measure to suffer total reflection and be absorbed, while the less inclined rays of the red and yellow would pass through and, illuminating the dark areas of total reflection, give the fibrous mass the brown tone. This explanation is based essentially on the same principle as that given by von Federov* for the pseudo-pleochroism which he observed in minerals containing thin parallel laminations. Only in this case there is no parallelism, the angular fibers lie in all directions, hence there is no apparent pleochroism and the mass appears of the same brown color in all positions and with, or without, polarized light.

It may be that in this lies the explanation of the brown and gray colors and pleochroic effects observed in spherulites in certain volcanic glasses by Cole,† but a search through the literature has not yielded to me any discussion of the frequent brown color of spherulites (or kaolin) though so commonly observed. Probably it is usually ascribed, if noticed, to some ferruginous pigment, to which in some cases it is undoubtedly due.

Some other features of interest which these spherulites show are as follows: In some, especially larger ones, hollow cavities appear; others have no cavities but a pronounced crack running through the center; often this crack passes along through several of them, and it is always rigorously parallel to the direction which the chain or line of spherulites makes (line of

* Min. Petr. Mitt., xiv, p. 569, 1895.

† Quar. Jour. Geol. Soc., xliv, p. 302, 1888.

flow). Where one has a cavity the ones immediately adjacent are apt to have the crack. In some places this crack has opened quite widely and an ellipsoidal or lenticular cavity is produced, bordered on either side by half spherulites extending into the glass. The bearing of these facts is discussed in a later place.

Another feature, quite similar to what is often seen in acid volcanic glasses, is the presence of cracks in the glass immediately surrounding the spherulites. These commonly start out from the edge of the spherulite, and especially from the place where two tend to intersect, and then curve, sometimes splitting and forming a Y. Usually after a short curve they stop, but quite often they continue in a long curve concentric to the outer surface of several adjacent spherulites and removed from it a small fraction of the total diameter of one of them (see fig. 3). It is owing to these concentric cracks surrounding them that the larger spherulites may be readily broken out of the glass and then appear with a thin, smooth skin, like varnish, coating them.

FIG. 3.



FIG. 3. Spherulites with cavities and cracks.

Stony Material.—In the material represented in the collection there are some pieces of a white lithoidal or porcelain-like appearance. They have a light greenish tone of color and a deeper green by transmitted light. A number of small vesicles or gas pores are here and there seen in the material. Under the microscope it is found to consist of glass filled with microlites; some of rather short, minute prisms of diopside with inclined extinctions and masses of feathery and fern-like forms of the same substance. There are also minute fibers whose extinction appears parallel and whose exact nature is doubtful.

OBSIDIAN.

One of the most interesting features of the collection is the presence of several specimens of jet black artificial obsidian, appearing quite similar in color, luster, and fracture to the natural obsidians from the Yellowstone Park, Mono Lake, Lipari Islands, and other well known localities. Flowage lines

or directions through the mass are indicated by parallel chains of little points around which the glass has a minute but different fracture and which thus interrupt the broad, smooth surfaces of the usual conchoidal areas.

The appearance of this black glass is so entirely unlike that of the ordinary light-green and transparent bottle glass that formed the flow that it is difficult to believe it is merely a modification of it, though positively so stated. It is, however, as will be presently shown, a curious modification of a light-green transparent bottle glass, though whether of the same melt as that which has been previously described as containing the spherulites seems doubtful. The doubt rests on chemical evidence. The first glass contains, as mentioned, only a small amount of iron, and a considerable proportion of magnesia, and diopside has crystallized from it; the qualitative analysis of the obsidian indicates much more iron, and while there is abundance of lime, magnesia is present only in minutest traces and as a result wollastonite has crystallized out in a particular layer, as will be described later. Unfortunately, in the lapse of time since the material was formed the possibility of obtaining more exact information concerning it and the conditions under which it was produced have been lost. If the statement accompanying the collection is to be trusted, then magmatic differentiation must have occurred, which seems hard to believe.

Considering the black color, it seemed at first as if the glass must have been of some other melt into which some unusual ingredient had entered which colored it black, or if a part of the flow, then one which had in some way imbibed a coloring constituent. Close inspection of a piece of this obsidian shows, however, that in a place where there are fractures, or cracks, penetrating it, if the mass is so turned to the light that the rays entering it are reflected back from the internal surface of the crack to the eye, the black color disappears and the glass, between the crack and the eye, assumes its normal sea-green transparent aspect.

The black color is due, then, not to a chemically diffused coloring matter, so to speak, in the sense that iron compounds color glass green, manganese purple, or cobalt blue, but is a mechanical effect of some kind, owing to which that light which strikes it and is not immediately reflected from the outer surface, penetrates it and is absorbed.

Many or most natural obsidians which appear black are found in thin section to be composed of a colorless glass, swarming with specks, or trichites, whose exact nature is unknown, but which many believe to be of magnetite. The idea involved is this: An obsidian is formed because the effusion and cooling have been so rapid that the ordinary rock con-

stituents have had no opportunity to begin to crystallize before the mass stiffened. But experience also shows that, in general, the more rapid the cooling the greater the number of centers of crystallization which will be set up. Now if anything should start to crystallize in magma under such conditions it would be the magnetite, ordinarily the earliest mineral of importance to form, and it would be therefore distributed through the glass in the shape of the finest dust acting megascopically as a mechanical pigment and coloring it black. The red color that many obsidians show may then be due to the complete oxidation of the magnetite to ferric oxide.

On the other hand, a study of a number of sections of various obsidians, and also of the literature, seems to indicate that the color may not be wholly due to magnetite. Zirkel,* in discussing it, considers that it is sometimes inherent in the glass (chemical so to speak) and is sometimes due to inclusions of minute size, which he describes. In the latter case the glass is colorless, and in the study of several obsidians of this character the writer has observed that the microlites, or trichites, have a higher index of refraction than the surrounding glass, as shown by Becke's method. On lowering the objective beyond the focal point they appear black, on raising it above they become illuminated and appear colorless. Consequently they are transparent and not magnetite. The greater the number of these incipient crystallizations there are, the blacker and less transparent the glass appears megascopically. The black color in this case then is due to light absorption. In one case where the slender microlites were arranged in parallel positions in streams, it was noticed that the section possessed a distinct pleochroism; when the ray vibrated across these streams it appeared colorless; when the long diameters were parallel to the ray it was distinctly brown. This is an effect of light absorption similar to that previously described under spherulites and doubtless produced in the same way. The black color of many obsidians then appears to be caused by the dispersion, total reflection, and absorption of light due to the presence of innumerable hosts of minute crystalline bodies of a higher refractive index than the glass in which they lie, such crystalline bodies being themselves colorless.

In the case of the artificial obsidian of Kane, with magnifications of 540 diameters, the microscope reveals the presence of bodies of indeterminate nature. They are so minute that no definite shape can be assigned to them, but they give a vague impression of being rudely octahedral. On lifting the objective they become strongly illuminated, on lowering they appear black. Thus they are transparent and of a higher

* *Lehrb. d. Petrog.*, vol. ii, p. 271, 1894.

index of refraction than the glass. While everywhere freely sprinkled through the field of view, as the stars appear at night in the sky, they cannot be said to swarm in the sense that, with reference to their own diameters, they closely approach one another. They exert no perceptible action on polarized light. To the absorption of light caused by the presence of these minute bodies, as with some natural obsidians, the black color of this variety of the Kane glass is ascribed.

Partly Crystallized Obsidian.—In one place there is a layer of the obsidian about 3 inches thick, which has partly crystallized. The black glass described above makes a rather clean and sharp contact with it. It is not now known whether this layer was above or below the pure glass one, but as it contains impurities on the side opposite the glass, and also on general principles, it is assumed as the bottom part of the obsidian. In the specimen it has a stony, not glassy, appearance; is of a very dark to blackish gray color, and is seen to be composed of a sort of felt of innumerable small slender-bladed crystals 2–4^{mm} long, which have a tendency to be arranged parallel to the extension of the layer. It has something of a rough resemblance to some hornblende schists.

There is no schistosity in the fracture however, which is rough and hackly. The thin section under the microscope is a very interesting one. It is composed of a pale brown glass, filled with beautiful crystallizations of the mineral wollastonite. While in general the mineral is developed as usual in long columnar forms, or plates parallel to the axis of symmetry, its growth has also been in such aggregates of sheaf-like, rosette-like, or feathery forms, that according to the way these are cut different effects are produced. The simplest case is shown in fig. 4, which gives a section parallel to b (010), across one of the bladed crystals. The faces in the zone of a (100) $\wedge$ c (001) are very

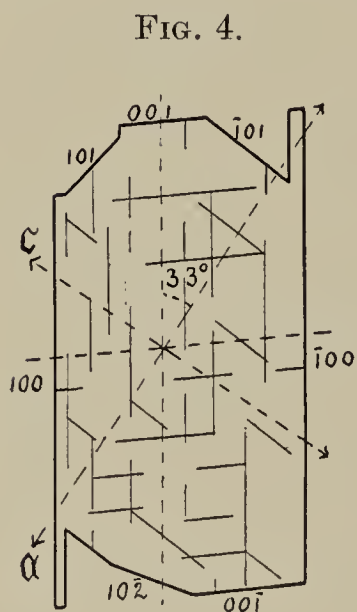


FIG. 4. Wollastonite, section parallel to b (010).

sharply developed, as may be seen from the following table of angles measured against the cross-hairs:

	Meas.	Calc.
β , a (100) $\wedge$ c (001)	84°	84° 35'
a' ($\bar{1}00$) $\wedge$ t ($\bar{1}01$)	50° 30'	50° 26'
a (100) $\wedge$ v (101)	42° 30'	44° 33'
a (100) $\wedge$ a (10 $\bar{2}$)	70°	69° 55'

The calculated angles are those given by Grosser* and the agreement is very good, except in $v(101)$, which was not so well developed as the other faces. The three cleavages parallel to 100, 001, and $\bar{1}01$ are excellent, as represented in the figure, their excellence being in the order given. The plane of the optic axes lies in the clinopinacoid and the bisectrix α makes an angle of 33° in the acute angle β with the vertical axis; Des Cloiseaux gives $32^\circ 12'$. The optical character is negative, α being the acute bisectrix. Since, according to Des Cloiseaux, the optic angle in air $2E = \text{about } 70^\circ$, it follows that one optic axis emerges almost perpendicular to $c, 001$, the other at an angle of about 16° to $a(100)$. Since both of these are good cleavages, it follows that when one examines the powder made by crushing the material, in convergent light under the microscope with crossed nicols, almost invariably each fragment exhibits the locus of an optic axis either just in, or just off, the field of view. Since the $a(100)$ cleavage is the best, it is mostly the latter case that obtains and in the blades the long direction is the one of least elasticity.

While these crystallographic and optical properties prove the nature of the mineral, its identity was confirmed by the fact that, when powdered, it dissolves readily in hydrochloric acid and yields gelatinous silica.

It will be noted in the drawing of the crystal shown in fig. 4 that the $a(100)$ faces are extended in a thin plate forming re-entrant angles; commonly these thin plates extend far beyond the main crystal and from each of the four corners, tapering off indefinitely; the cross section of the whole then shows an H with the vertical legs greatly extended. There may be other cross connections producing ladder-like affairs. It is also to be recalled that these extend as sheets perpendicular to the plane of the drawing, or along the b axis. Moreover the sheets are often curved and numbers of these extended plates are grouped into sheaves or rosette-like groups, and thus a variety of patterns are produced as these are cut by the section at various angles. The individual filaments as they appear in the section are commonly curved; if examined with a very high power it is seen that the curve really consists of a series of short minute straight pieces of crystal with wedge-shaped cracks between, continuity obtaining only along one edge. By this curving, and by repeated branching, arborescent, or plumose, forms are produced, and in places the glass between crossed nicols appears filled with them and seems like masses of magnificent ostrich plumes thickly scattered, the beauty of whose effect is greatly heightened by the use of the sensitive tint, which turns them brilliant blue and yellow.

* Zeitschr. f. Kryst., xix, p. 603.

These plumose forms, which are of remarkable delicacy and perfection, resemble the growths of augite in basaltic glass from Hawaii, described by E. S. Dana*; they differ from the growths in the pitchstone of Arran in being much larger, more perfect, and in the curved or curled character of the stems, thus resembling plumes rather than ferns. They never form complete spherulites, though in places the thickly-grouped, feather-like bunches partly resemble them.

Spherulitic Crystallization.

The vast majority of the natural spherulites occur in acid, that is to say, siliceous volcanic glasses, and are composed of quartz, or feldspars, or of these two minerals in various proportions. The reason for this is because it is especially in magmas of this nature that the relation between viscosity of magma and crystal growth, which is necessary for spherulitic crystallization and which is discussed later, is apt to occur. Spherulite crystallizations may occur in basic magmas and are known in the rocks called variolites,† but so far as the writer has been able to discover, no discussion of spherulites, as such, has been made which was not primarily based on material of the kind referred to. It is natural, therefore, that in these discussions the chemical character of the magma involved and the nature of the component minerals are largely held responsible as determinant factors for spherulitic crystallization. Since such natural magmas contain, as is well known, volatile constituents, especially water vapor, a considerable rôle has been ascribed to its agency in this connection. Thus Cross‡ ascribed the origin of the spherulites in a rhyolite studied by him to the presence of a colloidal condition in the magma, due to the antecedent formation of masses of opaline silica containing the elements of feldspar, which caused their formation and globular form. Iddings§ also, in his earlier discussions of spherulites, suggests that water vapor plays an important rôle in rendering certain places in the magma less viscous and therefore more susceptible to molecular movement and crystallization. This would explain the formation of crystalline spherulites in some places, while the surrounding magma solidified as glass although at the same temperature. He says: "Hence we may conclude that the influence of the absorbed water-vapor is to render the molecular mobility of the molten magma

* This Journal, xxxvii, 441, 1889.

† Pirsson, *Petrog. of Igneous Rocks of Little Belt Mts.*, 20th Ann. Rep. U. S. Geol. Surv., Pt. III, p. 532, 1900.

‡ Constitution and Origin of Spherulites in Acid Eruptive Rocks, *Bull. Phil. Soc. Wash.*, xi, 411, 1896.

§ *Bull. Phil. Soc. Wash.*, vol. xi, p. 446, etc., 1891.

greater at a given temperature in proportion to the amount of hydration, thus permitting the crystalline arrangement of the molecules in places of greater hydration, while the surrounding less hydrated portions are becoming too viscous."

In his latest discussion of spherulitic crystallization, Iddings* again refers the conditions controlling it in acid volcanic glasses to varying amounts of water vapor—as "probably dependent on viscosity, as affected by the gas contents of a magma." In these discussions, however, the underlying idea appears to be not so much an explanation of the assumption of the spherulitic *form*, or habit of growth, as of the production of local conditions which would favor crystallization and permit the formation of one component rather than another, for in spherulitic growths in the natural volcanic glasses one must deal with quartz and feldspar.

Spherulitic crystallization in the ultimate analysis is a question of crystal form or rather *habit*. The essential thing in a typical spherulite is that from a common center crystals grow in all directions whose elongation is excessive as compared with their breadth and thickness. They may be straight rods, or branching rays, or blades, or assume arborescent shapes, all of which occur in the Kane specimens, but always tending to elongate forms, thickly crowded. The suggestion of Cross tends to assume that the spherical shape or rather area was defined before crystallization actually occurred and is thus an explanation rather of the outward form than of the inward structure. It seems highly probable that the degree of hydration in the natural acid glasses affecting the viscosity, as suggested by the writers above, plays an important rôle in determining the conditions and places for spherulitic crystallization, but in the Kane glass this agency was not present and the complication of having two mineral substances to deal with is also wanting. The question here is simply one of the conditions which determined the assumption of a certain kind of crystal habit, and the answer, in the writer's opinion, is to be found in the degree of viscosity which had been attained at the time when the saturation of the solution with the diopside molecule reached the crystallizing point. Iddings† states that the habits of crystals depend in a large degree on the viscosity of the magma, long slender prisms and branching shapes being commonly developed when it is very viscous, though he does not explain why this is so. The writer offers this explanation for the slender fibers in the spherulites of diopside in the Kane glass. The pyroxene has a prismatic cleavage and is elongate

* Igneous Rocks, vol. i, pp. 231, 233, 1909.

† Igneous Rocks, vol. i, pp. 206, 216, 1909.

in the direction of this cleavage. It is not singular in this respect, for most minerals tend to be elongate, or columnar, in the direction of pronounced cleavages. In the direction normal to the cleavage faces the molecular network has a lesser amount of cohesive attraction than in other directions and hence the cleavage. We may therefore imagine that during the process of growth the amount of molecular tension or pull exerted by the crystal upon the unorientated molecules in the magma is greater toward the end face than toward the prism, or cleavage, faces. Hence the supply of molecules upon it is more rapid and the crystal grows faster in this direction. If now the viscosity of the magma rises to such a degree that the tension toward the side faces is not sufficient to overcome it and orientate the molecules while that upon the end face is sufficiently great, then the crystal will extend itself like a long rod, or fiber, until the growing viscosity puts a stop to further progress in this direction also. The crystallizing effect of the fiber end would also be aided by the fact, that as the molecules fall into position in the geometric network, or change from the liquid to the solid state, a certain amount of heat is liberated, tending to increase the mobility of the still unfixed adjacent molecules and to render them more susceptible to crystallographic orientation. The crystals then, like a wire with a hot end, bore out into the stiffening magma in all directions, and as conditions are uniform about them they cease simultaneously and the globular shape results. This relation of habit between viscosity and cohesive attraction is also well illustrated by the wollastonite crystals in the dark glass. They extend indefinitely along the b axis perpendicular to which there is no cleavage and are also tabular to the $a(100)$ face, parallel to which the best cleavage occurs. In the fibers of feldspar in spherulites in the volcanic rocks the elongation in the majority of cases is parallel to the clino axis, the direction of the two prominent cleavages. The instances cited where the elongation is parallel to the c axis* would tend to show that the molecular attraction to the $c(001)$ face in orthoclase is greater than that to the $b(010)$ face. The fact that large crystals and especially Carlsbad twins are often tabular or elongate on the c axis also shows this. It is generally considered that the cleavage $c(001)$ of orthoclase is better than that of $b(010)$, and this would appear to make these cases an exception to the general rule. It is not clear, however, judging from the views of the writers previously stated, that viscosity is the only factor to consider in these cases, as it is in the Kane glass, as a delicate balance between several different factors may have induced

* Iddings, Spherulitic Crystallization, Bull. Phil. Soc. Wash., vol. xi, p. 456, 1891.

this particular form. Nor does the writer wish to affirm as a positive rule that in all minerals the attraction causing growth is less towards a pronounced face of cleavage than in other directions. It does, however, appear to be a rather general one.

In addition to the elongation of the fibers in spherulites there is also the branching to be taken into account. The more rapid growth of the corners and edges of crystals, due to their commanding a larger portion of the space which is supplying the crystallizing material and thus producing branching and skeleton growths, was brought to attention by Lehmann* and further elaborated by Rosenbusch† and needs no further discussion here. In the treatment of the subject by these authors, however, it is tacitly assumed that the molecular attraction towards all faces of the growing crystal is the same, or at least there is not mentioned anything to the contrary, and the view previously expressed by the writer, that this may be different on different faces, brings into play another factor.

That the molten glass had attained a considerable degree of viscosity before crystallization began is clearly indicated by the spherulites seen in figs. B and C of the plate, since it was great enough to support these denser bodies and prevent them from sinking to the bottom.

That the formation of the spherulites was a comparatively rapid process, after crystallization once started, is plainly shown by their occurrence in the manner figured in A of the plate. They were not present, of course, in the molten glass in the furnace before breakage occurred, and their appearance here in flow lines proves they had formed before flowage motion of the glass had ceased. However long a time viscous flowage may continue in larger masses of lava, in this small body of glass it must have had a relatively short period.

From the foregoing discussion it appears that the production of spherulites in an anhydrous molten glass depends upon crystallization starting from a center and proceeding outwardly in all directions at a time when the molten solution had attained such a degree of viscosity as to control the crystal habit and also upon the composition being such as to produce minerals which naturally grow in columnar forms. The time interval between this point and that where the fall of temperature increases the viscosity to such a degree as to prevent further molecular movement evidently controls the size of the spherulites. In the case of the huge spherulites described by Cross‡ from Colorado this time interval must have been relatively long.

* Ueber das Wachsthum der Krystalle, *Zeitschr. f. Kryst.*, i, 462, 1877.

† *Phys. der Min.*, 1885, p. 26, 4th ed., vol. 1, 361, 1904. ‡ *Loc. cit.*

In a sheet of molten glass the planes of cooling descend vertically into the mass so that variations of temperature from point to point become much more marked in this direction than in a horizontal one. It is also true that in the change from the liquid to the solid condition a more or less considerable contraction of volume ensues. Further, the force of crystallization is very powerful within the distance in which it acts,* and in the final stage of viscosity before the capability of molecular movement ceases the tension on the growing crystal faces must be very strong and, *per contra*, on the adjacent areas of unorientated molecules. Taking these facts into consideration, it is clear that especially toward the end of the process of spherulitic crystallization, these bodies and the glass surrounding them will be subjected to stresses which are most marked in vertical directions. Unable to withstand the tension, they may rupture, giving rise to horizontal, or longitudinal, cracks or even be pulled apart so that ovoid, or spherical, cavities are opened within them, as illustrated in fig. 3. Or the tension between them and the surrounding glass may be relieved by tangential, or radial, cracks in the latter, as also illustrated and described. Thus the layers of spherulites spread through the glass in bands by flowage become elements of inherent weakness and along them it splits into plates and thus has a laminated structure. This phenomenon is also noticed in natural rhyolite glasses, like those from Lipari and the Yellowstone Park, which cleave readily along the bands of spherulites. Iddings,† in discussing the laminated nature of such rocks, attributes it to non-homogeneity in different parts of the magma, produced by variable amounts of contained water vapors, which unlike portions by the spreading out action of flowing lavas become distributed in thin sheets. Hence arise layers of different degrees of consistency, crystalline character, etc., which condition the banded structure and cause lamination. The Kane glass, however, shows that the same lamination, though not perhaps in so high a degree, can be formed in the cooling of an anhydrous magma and that the water vapor, except where it causes layers of bubbles, as in pumice, must be an indirect rather than a direct agent in producing lamination in that it promotes more favorable conditions for crystallization.

Differentiation.—In the clear glass containing relatively few small spherulites there is a non-homogeneous quality which shows itself by drawn out streaked lines and layers, these being nowise different in color or consistency, but having dif-

* Becker and Day, Linear Force of Growing Crystals, Wash. Acad. Sci. Proc., vol. vii, p. 283, 1905.

† This Journal, vol. xxxiii, p. 43, 1887; Igneous Rocks, vol. i, p. 243, 1909.

ferent refractive indices, and thus becoming visible by their action on light, in the same manner that heated air-currents are visible above a source of heat, or differing currents of salt laden solutions are seen in a liquid. These streaks are small and fine and are parallel to one another, and to the chains of spherulites, in the direction of flow. Since the refractive index varies in the different layers there must be a difference in composition to occasion it. The difficulty of obtaining glass of uniform composition, through a tendency to separate into unlike portions, is one well known to makers of lenses and other users of optical glass and has been frequently described. It needs no further mention here beyond the comment that this case adds another to those which have been cited by others as a proof that the instability of molten silicate solutions furnishes a presumptive proof of the possibility of magmatic differentiation on a larger scale.

If we accept the statement, which cannot unfortunately be now verified, that the black obsidian is really a part of the same glass flow, a more striking instance of differentiation is shown in that the clear glass is rich in magnesia and poor in iron oxide while in the obsidian the reverse is the case. This difference explains very clearly why diopside crystallized out in the one and wollastonite in the other. But such a movement, provided we suppose the original molten solution to have been homogeneous, whereby magnesia and ferrous oxide are concentrated in opposite directions, while one would hesitate to say it was impossible, from all our experience gained in the study of rock-masses in which these oxides move together, seems very unlikely to say the least. And on the other hand, we do not know, in the production of glass on so large a scale, whether a sufficiently high temperature was maintained long enough to permit the molten solution to assume conditions of uniformity throughout its mass, if, on account of a difference of materials used in the making, uniformity was not present to begin with. Viewed from this standpoint, it is possible that the obsidian was part of the same flow. At all events, the material seems to indicate the possibility of obtaining in this direction, artificially, some light on the, at present, mysterious process, or set of processes, known as differentiation.

Composition of Minerals.—The use of the terms diopside and wollastonite in this paper is of course only a general one and it is not assumed that these substances are necessarily present in a pure condition. From the splendid results which have been achieved in recent years by Dr. Day and his co-workers in the Geophysical Laboratory of the Carnegie Institution concerning the properties of the lime and magnesia silicates, and the conditions under which they are formed, and

which have been published in this Journal,* it has been shown so clearly that diopside and wollastonite, as produced from molten solution, may contain variable amounts of lime and magnesia metasilicates in solid solution, that it would seem quite possible that the diopside in the Kane glass is far from being pure in composition. The analytical test proves that the wollastonite is relatively a pure compound, and the optical data, so far as they go, agree with this view.

It is evident from the works quoted that the temperature of the glass, when the wollastonite crystallized, must have been lower than 1190° , since this is the inversion point of the mineral to pseudo-wollastonite, which alone exists above that temperature and up to 1512° , its melting point. The melting point of diopside is 1380° and the temperature of the molten solution was therefore originally above this point; this of course is to be expected, even though a flux is used to help carry the quartz sand and lime carbonate into solution.

Summary.—The study of the accidental flow of molten bottle-glass at Kane, Penn., has brought out the following chief points:

That spherulites of varying size and character and consisting of diopside may be formed in an anhydrous molten solution by rapid cooling.

That the spherulitic type of crystallization appears to be conditioned by the relation of crystal habit and properties to the viscosity of the magma. The spherulites are of rapid growth.

That the brown color, which many spherulites exhibit by transmitted light, is a phenomenon of light absorption.

That obsidian may be artificially produced from a clear glass and that its black color is a phenomenon of light absorption.

That artificial wollastonite may exhibit certain characters which are described.

Sheffield Scientific School of Yale University,
New Haven, Conn., April, 1910.

* Day, Shepherd and Wright, *The Lime-Silica Series of Minerals*, vol. xxii, pp. 265–302, 1906. Allen, White and Wright, *On Wollastonite and Pseudo-wollastonite, Polymorphic Forms of Calcium Metasilicate*, vol. xxi, pp. 89–108, 1906. Allen, White, Wright and Larsen, *Diopside and its Relation to Calcium and Magnesium Metasilicates*, vol. xxvii, pp. 1–47, 1909.



A



B



C

SPHERULITES IN ARTIFICIAL GLASS.



3 0112 072839019